DOI: 10.15826/chimtech.2015.2.4.028

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Phase equilibria and thermodynamic properties of oxide systems on the basis of rare earth, alkaline earth and 3d-transition (Mn, Fe, Co) metals. A short overview of.

Review is dedicated studies of phase equilibria in the systems based on rare earth elements and 3d transition metals. It's highlighted several structural families of these compounds and is shown that many were found interesting properties for practical application, such as high conductivity up to the superconducting state, magnetic properties, catalytic activity of the processes of afterburning of exhaust gases, the high mobility in the oxygen sublattice and more.

Keywords: *phase equilibrium; manganites; isobaric-isothermal diagrams; solid solutions*

Introduction

The studies of phase equilibria in the systems based on rare earth elements and 3d transition metals and thermodynamic parameters of the oxide phases formed in these systems was initiated by Vladimir Mikhailovich Zhukovsky in 1977 under the direct supervision of Alexander Nikolaevich Petrov, as the development of contractual issues, conducted with an experienced company GIREDMET. The works on the study of the system Sm–Co–O and properties of oxide phases formed in system were then extended to other rare earth elements (REE) [1–8] and 3d transition metals [9–13]. A characteristic feature of these systems is the formation of oxide phases with perovskite structure AVO_3 and related. The partial substitution of rare earth elements in alkaline earth metals (AEM) leads to significant change of properties and they found a wide range of interesting for practical applications of the properties such as high conductivity up to the superconducting state, magnetic properties, catalytic activity of the processes of afterburning of exhaust gases and a variety of redox reactions, high mobility in the oxygen sublattice and more. In addition, partial substitution in the A-sublattice under constant 3d-cation in the systems Ln–T–O allows to stabilize the structure, which

in the given conditions (temperature and oxygen pressure) are thermodynamically unstable. Therefore, further development of investigations of phase equilibria and thermodynamic stability of complex oxides were targeting the systems Ln–M–T–O (where Ln = REE, M = Ca, Sr, Ba; T = Mn, Fe, Co, Ni, Cu). When a certain percentage of similarity (in all possible formation of a phase with perovskite structure $LnTO_{3\pm\delta}$) these systems still have a noticeable and distinctive features depending on the nature of the components.

Phase equilibrium in systems with T = Mn

The significant difference of perovskite phases in the manganese-containing systems Ln–Mn–O is that the oxygen content in them exceeds the stoichiometric air $LnMnO_{3+\delta}$. In fact, the oxygen sublattice is complete and the non-stoichiometry is realized by vacancy disordering of cationic A- and B-sublattices and from a structural point of view it is more correct to represent the formula of such manganite $Ln_{1-y}Mn_{1-y}O_3$ [14–24]. Another feature distinguishing Mn-containing systems, is an obvious area of homogeneity on the metal components $Ln_{1-x}MnO_3$ and $LnMn_{1-x}O_3$ [13, 25–29]. During the replacement of REE in alkaline earth metals (Ca, Sr, Ba) are formed solid solutions $Ln_{1-x}M_xMnO_{3\pm\delta}$. The limits of substitution depend both on the nature AEM, so from external conditions (T, PO_2). In Fig. 1 and 2 show the isobaric-isothermal diagrams for the systems La–M–Mn–O (M = Ca [30], Sr [31, 32]), respectively.

The complex relationship between the limit of heterovalent substitution of lanthanum by strontium in $La_{1-x}Sr_xMnO_{3\pm\delta}$ with oxygen (3±δ) when the pressure decreases is well illustrated in Fig. 3.

The charge compensation during replacement of Sr^{2+} for La^{3+} may occur by increasing the degree of oxidation of manganese or by reducing the oxygen content. A significant reduction of oxygen content in the first stage reduction of pressure (0.21–10^{-9} атм) [14, 33] leads to the possibility of increasing content of strontium in boundary composition (x). With further decreasing oxygen pressure 10^{-9}–10^{-13} атм loss of oxygen by solid solution slows down, the dependence $\delta = f(Po_2)$ reaches a plateau [14, 33] and the decrease of the degree of oxidation of manganese is achieved by reducing the solubility of strontium in $La_{1-x}Sr_xMnO_{3-\delta}$. Enriched with strontium solid solutions $La_{1-x}Sr_xMnO_{3-(0.5+x)/2}$ $(0.67 \le x \le 1)$ with oxygen vacancies ordered in a 6-layer perovskite-like structure, at low oxygen activity (in the presence of NaH) and at low temperatures (not higher than 400 °C) are described in [34]. It should be noted that the equilibrium implemented with decreasing pressure of oxygen dur-

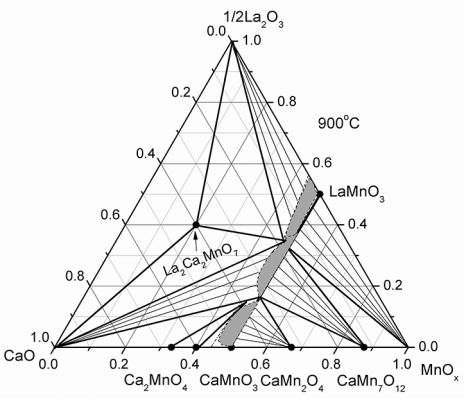
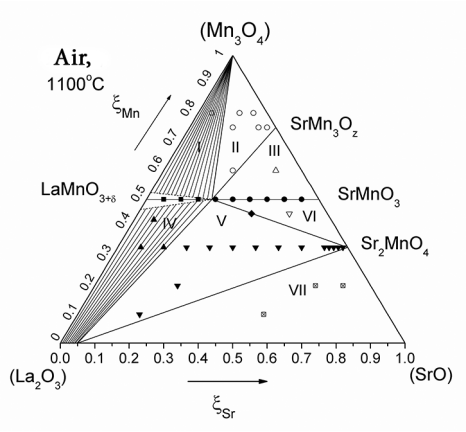


Fig. 1. Isobaric-isothermal section phase diagrams of La–Ca–Mn–O at 1100 °C in air [30]



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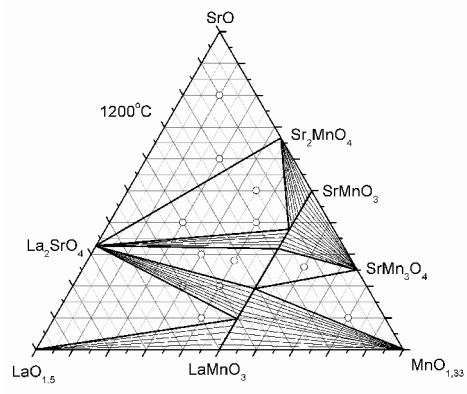

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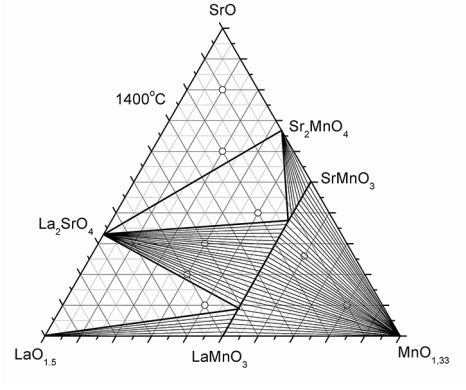

c

Fig. 2. Isobaric-isothermal section phase diagrams of La–Sr–Mn–O in air at 1100 °C [31] (a); 1200 °C [32] (b); 1400 °C [32] (c)

ing the decomposition of solid solutions $Ln_{1-x}Sr_xMnO_{3-\delta}$ is monovariant, and therefore a method of measuring EMJ in cells with solid electrolyte in its classical version can be applied with certain reservations, and the interpretation of the results obtained in [35, 36] is in doubt. The use of more redox conditions allows to get a phase belonging to a homologous series Ruddlesden-Popper $A_{n+1}B_nO_{3n+1,}$ for example, n=1 $((La_{1-x}Sr_x)_2MnO_4$ [31], $n=2$ $La_{1+x}M_{2-x}Mn_2O_7$ (M=Ca, Sr) [37–39]. The full chart for the system La–Ba–Mn–O is not known, systematically studied only cut $LaMnO_{3\pm\delta}$ – $BaMnO_{3-\delta}$, solid solutions $La_{1-x}Ba_xMnO_{3\pm\delta}$ at 1100 °C in air are formed in the interval $0\le x\le 0.3$ [40–42]. Similarly, Sr-substituted, the barium content may be increased to more reducing conditions (lower oxygen pressure, increasing temperature) up to $x=0.5$, but there is the effect of streamlining the education phase double perovskite $LaBaMn_2O_{6-\delta}$ [43]. Streamlining A-subject-cations: La

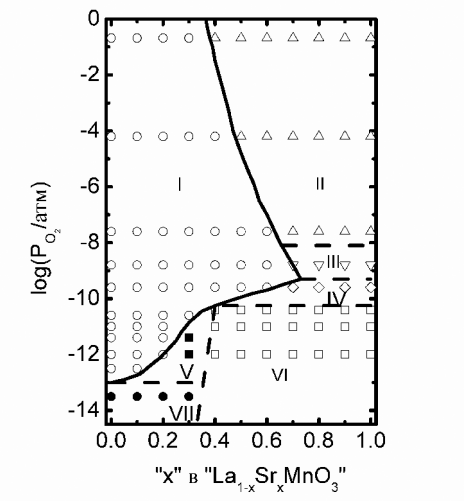

Fig. 3. Section "-composition" phase diagram of the system La–Sr–Mn-O along the line of the $LaMnO_{3-d}$ - $SrMnO_{3-d}$ at 1100 °C [31]

and Ba are arranged in alternating layers, doubling, thus the unit cell along the C-axis and oxygen vacancies, are concentrated in the plane La-O, thus forming the more complex superstructures [43, 44].

The systematic study of phase equilibria for other REE have not been conducted, there have been studies of individual compositions $Ln_{1-x}MMnO_{3\pm\delta}$ [45-48], including double-layer cation-ordered $LnBaMn_2O_{5+\delta}$ [49–51]. Like La-containing systems and the complex oxides Ruddlesden-Popper series $(Ln,M)_3Mn_2O_7$ [52–58], $(Ln,M)_2MnO_4$ [58–61] were obtained. Another class of compounds based on rare-earth elements, calcium and manganese $Ln_2Ca_2MnO_7$ was obtained using high pressures (4 GPA in the presence of $KClO_4$), the structure of which is constructed by alternating hexagonal perovskite-like layers and graphite-like Ca_2O-layers [62, 63].

Phase equilibrium in systems with T = Fe

The results of a systematic study of phase equilibria in systems La–M–Fe–O (M = Ca, Sr) at 1100 °C in air are presented in Fig. 4, 5 [64].

The solid solutions $La_{1-x}Sr_xFeO_{3-\delta}$ crystallize in the perovskite structure with two types of distortion: orthorhombic ($0 \le x \le 0.2$) and starting with x=0.5, rhombohedral, which are reduced, allowing to describe the structure of a cubic cell in the range of compositions of $0.6 \le x \le 0.8$ [64]. The homogeneity regions substantially depend on the oxygen content and, therefore, the conditions of processing/receiving, the influence of which increases with increasing content of strontium. For example, at a temperature of 1300 °C-installed the homogeneity regions were as follows: orthorhombic cell with space group *Pbnm* exists in the range of compositions $0 \le x \le 0.2$, the rhombohedral cell ($R\bar{3}c$) is at $0.4 \le x \le 0.7$, cubic ($Pm3m$) is at $0.8 \le x \le 1$ [65, 66]. Thermogravimetric studies allowed us to assess the thermal stability of $La_{1-x}Sr_xFeO_{3-\delta}$ in an atmosphere of 95 % He+5 % H_2, which decreases with increasing content of strontium [66].

Numerous studies of properties of compounds with the general formula $M_2LnFe_3O_{8+\delta}$ (M = Ca, Sr) [67–71], (which otherwise can be represented as $Ln_{0.33}M_{0.67}FeO_{3-\delta}$), obtained, as a rule, at

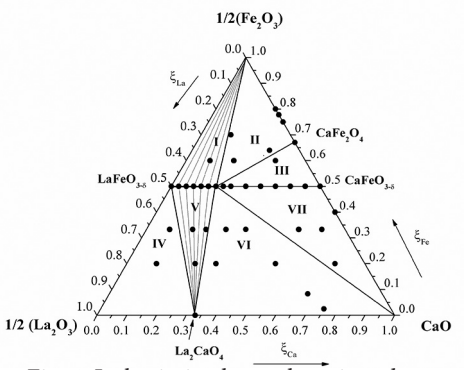

Fig. 4. Isobaric-isothermal section phase diagrams of La–Ca–Fe–O at 1100 °C in air [64]

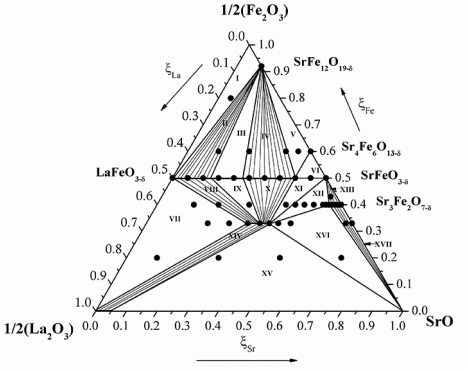

Fig. 5. Isobaric-isothermal section phase diagrams of La–Sr–Fe–O at 1100 °C in air [64]

high temperatures 1200–1400 °C in air, and in some cases processed in an inert atmosphere do not give unfortunately, a clear answer to the question is this structure unique or is one of the homogeneity region, although the observed domain structure of the material confirms the predominant cation ratio M/Ln=2/1 [67]. The ordering of cations in the A-sublattice $Ln_{0.33}Sr_{0.67}FeO_{3-\delta}$ can be correlated with oxygen non-stoichiometry and the domains with a possible streamlining of the La/Sr = 1/2 in the oxide with δ = 0–0.1, observed by electron microscopy, are not recorded under δ = 0.15–0.33 [70, 71]. Another confirmation of the relationship of the structure and content of oxygen may be the results of determining the oxygen non stoichiometry and structural analysis as a function of temperature for $Sr_2LaFe_3O_{8+y}$ [68]. The partial replacement of lanthanum for strontium stabilizes the first term of the series Ruddlesden-Popper $La_{1-x}Sr_x)_2FeO_4$ [64] and at temperatures above 1200 °C begins the formation of next $La_2SrFe_2O_7$ [72]. Quasi-binary section of the chart $LaFeO_3$ – $LaSrFeO_4$ is presented in Fig. 6 [72].

In addition to these phases the starting forming of the third member of the homologous series n=3 $LaSr_3Fe_3O_{10-\delta}$ [73] is fixed, the oxygen content which varies in the range $0.1 \le x \le 0.8$ depending on the conditions of obtaining and processing [74]. The systematic studies of phase equilibria in systems Ln–(Ca, Sr)–Fe–O so far have not been conducted. The separate solid solutions were received and investigated, for example, $Nd_{1-x}Sr_xFeO_{3-\delta}$ ($0.6<x<0.8$) [75], $Pr_{1-x}Sr_xFeO_{3-\delta}$ [76], $Sr_{1+x}Nd_{1-x}FeO_{4-y}$ [77]. In addition, as La-containing compounds in the systems Ln–Sr–Fe–O was recorded the formation of layered phase composition $LnSr_2Fe_2O_7$ (Ln = Nd, Eu) with the tetragonal symmetry [78].

The information on phase equilibria in the system La–Ba–Fe–O is virtually little it is known about the possibility of obtaining solid solutions $La_{1-x}Ba_xFeO_{3-\delta}$ [79, 80] and a layered phase $BaLa_2Fe_2O_7$ [81]. As in Mn-containing systems, a significant difference in size of the barium and REE with sequence number greater than that of lanthanum leads to the formation of ordered layered structures. Much attention is paid to investigation of the conditions of obtaining and properties of phases with the general formula $LnBa_2Fe_3O_{8+w}$ [82–84]. As noted above, the receipt of such phases is essentially determined by the processing conditions (temperature and oxygen pressure) and the possibility of ordering in the cation sublattice is associated with both the oxygen content and the difference of radii of A-cation [85–87]. The getting dulaine ordered structures $LnBaFe_2O_{5+\delta}$ is possible at temperatures above 620 °C and low partial pressure of oxygen (P_{O_2} = $10^{-12.44}$ – $10^{-29.4}$ atm) [88–90]. For Ln = Sm at atmospheric pressure, the existence of five-layer oxide phases $Ln_{2-\varepsilon}Ba_{3+\varepsilon}Fe_5O_{15-\delta}$ [91] is determined.

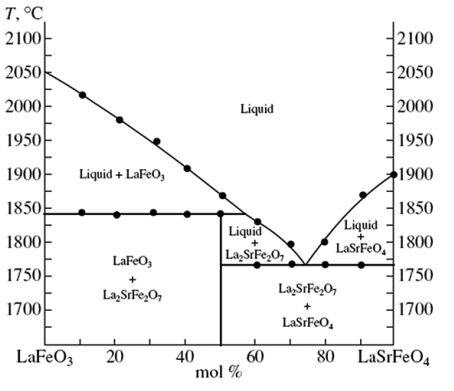

Fig. 6. Quasi-binary section of the chart $LaFeO_3$ – $LaSrFeO_4$ at atmospheric pressure [72]

Phase equilibrium in systems with T = Co

Phase equilibria in systems La–M–Co–O (M = Ca, Sr, Ba) been studied quite extensively in several papers [92-96] at different temperatures and atmospheric pressure (Fig. 7– 9).

The region of homogeneity of substituted lanthanum cobaltites $La_{1-x}Ca_xCoO_{3-\delta}$ depends on the conditions of heat treatment. The annealing of samples at atmospheric pressure and 885 °C allowed us to obtain single-phase samples in the range of compositions $0 \le x \le 0.2$ [93] at 1100 °C by the authors [92, 95], the boundary of existence was drawn between x =0.3 and x =0.4, while after annealing the oxides at 1200 OC region of existence of solid solutions extends up to x = 0.5 [97, 98]. The solid solutions $La_{1-x}Ca_xCoO_3$ crystallize in the orthorhombic cell, in this case the reduction of the rhombohedral distortion with increasing x values [97] is observed. Similarly, the introduction of strontium and barium in the sublattice of $LaCoO_3$ leads to a reduction of rhombohedral dis-

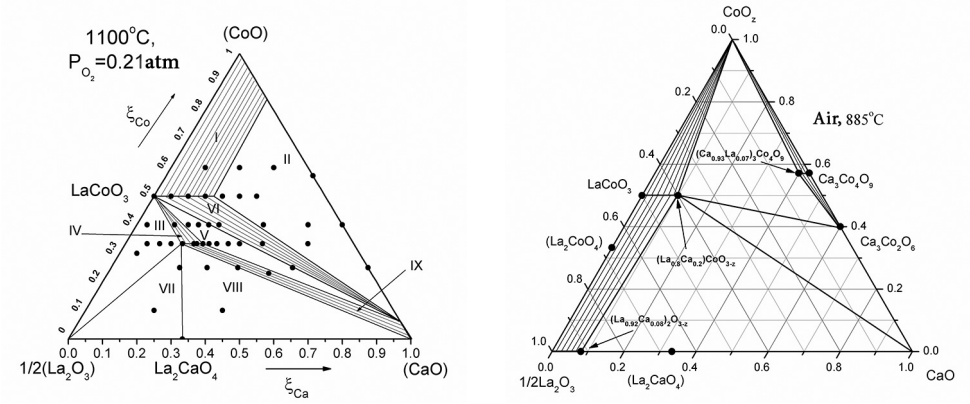

Fig. 7. Isobaric-isothermal section phase diagrams of La–Ca–Co–O on the air at 1100 °C [92, 95] (a); 885 °C [93] (b)

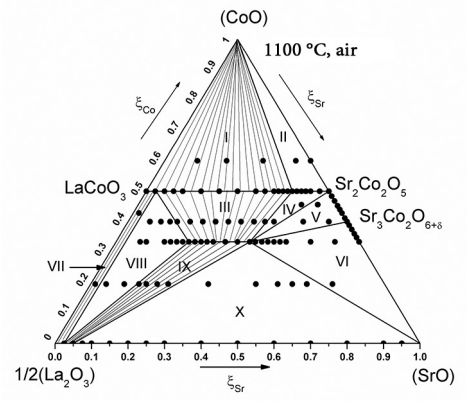

Fig. 8. Isobaric-isothermal section phase diagrams of La–Sr–Co–O at 1100 °C in air [94]

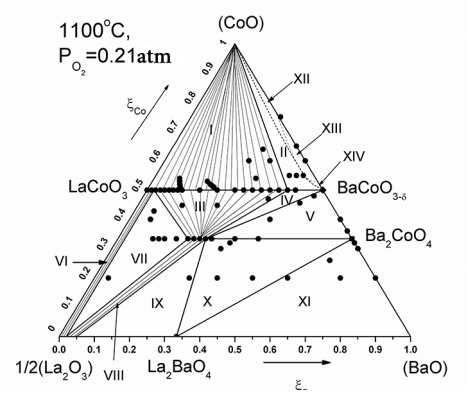

Fig. 9. Isobaric-isothermal section phase diagrams of La–Ba–Co–O at 1100 °C in air [92, 96]

tortion in the range $0.0 \le x < 0.5$ [94–96, 99] and the oxides with $0.5 \le x < 0.65$ (M = Sr) и $0.5 \le x \le 0.8$ (M = Ba) have ideal cubic structure. A further increase in the strontium content of $0.65 \le x \le 0.8$ leads to the appearance of orthorhombic distortions of the cubic structure [94]. The assignable region of homogeneity $La_{1-x}Ca_xCoO_{3-\delta}$ is considerably less than was found for Sr – and Ba-substituted lanthanum cobaltites. This may be due in part to a dimensional factor, because reducing the size of cation in position *A* reduces the resistance perovskite phases [100], but mainly with the fact that the valence state of cobalt ions determines the thermodynamic stability of these systems [94].

In air at 1100 °C phase La_2CoO_4 is not formed [12, 101]. The introduction of alkaline earth metal in the lanthanum sublattice increases the average oxidation state of cobalt in the solid solution $(La_{1-y}M_y)_2CoO_4$, thereby stabilizing the phase with the structure of the K_2NiF_4 type [93–96, 102]. The regions of existence of solid solutions at T = 1100 °C and =0.21 ATM are in the range of compositions $0.25 \le y \le 0.3$ for M = Ca [92, 95]; $0.30 \le y \le 0.55$ for M = Sr [94]; $0.300 \le y \le 0.375$ for M = Ba [92, 96].

The results of comprehensive study of phase equilibria in systems La–M–Co–O (Ln = Nd, Sm; M = Ca, Ba) are presented in fig. 10, 11, 12 [103, 104].

The information about the intermediate compounds formed in the systems Ln–M–Co–O (M = Ca, Sr) is rather limited. At partial substitution of calcium to REE in the cobaltites $Ca_{3-x}Ln_xCo_2O_6$ ($0 \le x \le 0.15$) [105, 106] and $Ca_{3-x}Ln_xCo_4O_9$ ($0 \le x \le 0.15$) [103] there is an increase in the decomposition temperature of the respective oxides. The region of existence of solid solutions on the basis of orthogonality neodymium $Nd_{1-x}Ca_xCoO_{3-\delta}$ is limited to the value of $Nd_{1-x}Ca_xCoO_{3-\delta}$ x =0.25 [103]. In a series of "$SrCoO_{3-\delta}$" – "$LnCoO_{3-\delta}$" are formed several oxide phases crystallized in different structural type, depending on the nature of the REE [106-109] (Fig. 13).

The phases related to homological series Ruddlesden-Popper $Ln_{2-x}M_xCoO_{4-\delta}$ (M = Ca, Ln = Pr - Gd; M = Sr, Ln = Pr, Sm) [103, 111-113] have been obtained and studied in air.

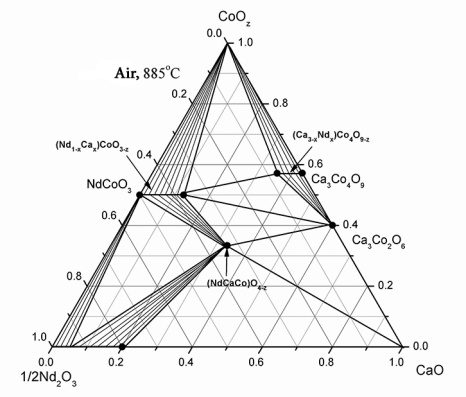

Fig. 10. Isobaric-isothermal section of the phase diagram of Nd–Ca–Co–O at 885 °C in air [103]

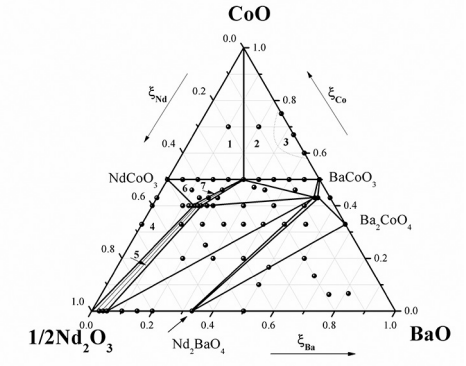

Fig. 11. Isobaric-isothermal section of the phase diagram of Nd–Ba–Co–O at 1100 °C in air [104]

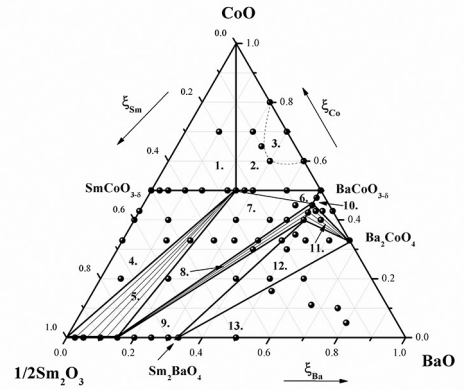

Fig. 12. Isobaric-isothermal section of the phase diagram of Sm–Ba–Co–O at 1100 °C in air [104]

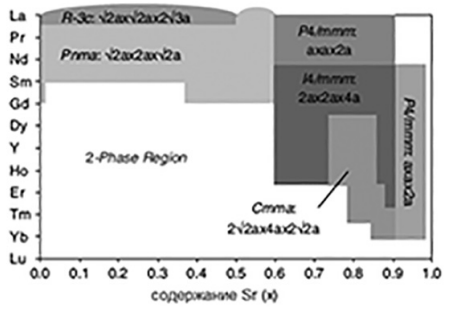

Fig. 13. Phase diagrams of perovskite-like structures $Sr_xLn_{1-x}CoO_{3-\delta}$ at 300 K [109].

When considering systems Ln–Ba–Co–O much attention is paid to bilayer ordered perovskites $LnBaCo_2O_{5+\delta}$ [114-121]. Unlike iron- and manganese-containing systems, the compounds with similar structure are thermodynamically stable at atmospheric pressure. Depending on the radius of the REE and the conditions of synthesis of oxides, the formation of multiple types of superstructures, which are characterized by alternating planes containing atoms of rare-earth metals or barium, and of the ordering of oxygen and vacancies in the layers LnO_δ [114].

For a number of REE the separate compounds $BaCo_{1-x}Sm_xO_{3-\delta}$ ($0.1 \le x \le 0.2$) [104], $Nd_{3-x}Ba_xCo_2O_7$ ($0.70 \le x \le 0.80$) [104] and related to the phase type Ruddlesden–Popper, $Ln_2BaCo_2O_{7-\delta}$ (Ln = Sm, Eu, Gd), [121, 123] were obtained and described.

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